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(54) Method of Recovering Chemicals and Heat in Sulphate Spent Liquor by Means of Al $(OH)_3$ or $TiO_2.n.H_2O$ Circulation and Gasification of the Waste Liquor

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A method of recovering chemicals and heat in sulphate spent liquor by means of $Al(OH)_3$ or $TiO_2.n.H_2O$ circulation and gasification of the waste liquor

Abstract of the Disclosure

The invention relates to a method of recovering chemicals and heat in sulphate spent liquor, wherein evaporated black liquor is granulated by means of circulated $Al(OH)_3$ and $NaAlO_2$ or $TiO_2.n.H_2O$ and Na_2TiO_3, whereafter the granules are fed into a spent liquor gasifier where the temperature is from 700 to 1250°C. The granules which do not contain carbon, organic matter or sulphur are discharged from the gasifier, cooled with air and crushed, whereafter a part of the sodium aluminate or sodium titanate formed, if desired, is circulated to granulation and the remainder is dissolved in water. Hereby either NaOH and $TiO_2.n.H_2O$ is formed which is precipitated or recirculated, or, when using $Al(OH)_3$ circulation, an alkaline aluminate solution which can be directly used as absorption solution for H_2S or cooking liquor in sulphate cooking. $Al(OH)_3$ can also be precipitated from the solution and recirculated to granulation, whereby the remaining mother liquor mainly containing Na_2CO_3 is passed to causticizing. The gas mixture obtained from the gasification of spent liquor is cooled, whereafter H_2S is absorbed from the gas into the NaOH solution or directly into the alkaline aluminate solution. The obtained solution is passed to the preparation of cooking liquor, and the flue gas is burned.

Method for the preparation of pulp and for the recovery of chemicals

The invention is concerned with an alkaline pulp cooking in which sodium aluminate and sodium sulphide are used as cooking chemicals. More specifically, the invention is concerned with a method for the preparation of pulp and for the recovery of chemicals, whereby hardwood or softwood chips are cooked by means of a sodium-sulphide-containing aqueous solution of sodium aluminate in a conventional sulphate pulp cooker under standard conditions. The method is characterized in that the spent liquor separated from the cooking is, after evaporation, fed into a gasifier, wherein the temperature is 700 to 1250°C, the hot inorganic matter is removed out of the gasifier, cooled by means of the air required for the gasification, crushed and dissolved in water, and the alkaline aluminate solution obtained is used as an absorption solution for the H_2S contained in the gas generated in the gasifier, whereby a solution is obtained which contains 1 to 4 percent by weight of Na_2S and NaHS as well as 5 to 20 percent by weight of $NaAlO_2$ and which is as such, without separate causticizing, suitable for the cooking of pulp, and the obtained gas, free from hydrogen sulphide, is burned in a suitable boiler.

In the method in accordance with the invention, the cooking chemicals can be recirculated to the cooking in the regenerated form without a separate causticizing step. The use of aluminate as an auxiliary chemical in autocausticizing is in itself known in the sulphite process, in the so-called Sonoco process (Cook, W.R., Tappi 57 (1974), 9, pp. 94-96), as well as in the two-stage burning according to the Finnish Patent No. 62,562. Aluminate has also been suggested to be added to sulphur-free alkaline cooking (so-called soda cook) (see U.S. Patent 2,601,110), whereby, however, about one half of the alkali must be added in the form of sodium hydroxide,

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which makes autocausticizing impossible.

In the paper Paperi ja puu No. 2, 1979, pp. 98-103, it is stated that sodium aluminate is not a sufficiently strong base in order that it could be substituted for sodium hydroxide in cooking.

In the paper Paperi ja puu No. 3, 1978, pp. 129-132, it is stated that sodium-aluminate autocausticizing can be used only in sulphur-free cooking.

In the following, reference will be made to the attached Figure 1, which shows the circulation of $Al(OH)_3$ and the gasification of the spent liquor in the method in accordance with the invention.

The evaporated black liquor 2 obtained from the cooking 1 is granulated with circulated $Al(OH)_3$ and $NaAlO_2$ into granules of 10 to 20 mm in a granulating drum 3, in a way known per se, whereafter the granules are fed into the gasifier 4 for spent liquor, wherein the temperature is 700 to 1250°C. Because of the high melting point of the sodium aluminate formed, the operation is all the time carried out in the solid phase. Gasification of spent liquor is known, e.g., from the SCA-Billerud process (STFI Meddelanden, serie D7, 1976, pp. 132-138). The hot granules, which no more contain organic material or sulphur, are discharged from the bottom of the gasifier and cooled, for example, by means of a fluidized bed cooler 5. The cooling is effected by means of the air needed for the gasification. Hereafter, the granules are crushed and, if desired, a part of the sodium aluminate formed is circulated to granulation 1. The rest of the sodium aluminate is dissolved in water 6, and, if desired, the material insoluble in water can be separated and recirculated.

The gas mixture obtained from the gasification of the spent liquor is cooled in a waste heat boiler 7 and possibly in addition by means of a spray cooler. The H_2S is absorbed straight into the alkaline aluminate solution. This is a well-known technique,

which can be carried out with very small H_2S losses. In the absorption device 8, H_2S reacts with NaOH, whereby a solution is obtained which contains Na_2S, NaHS, and $NaAlO_2$; the H_2S-free gas is burned in a suitable boiler.

Unexpectedly it has been found that the solution obtained from absorption of H_2S is as such, without separate causticizing, suitable as a cooking liquor for pulp. In this way, it is possible to simplify the chemical circulation of the sulphate pulp process without deterioration of the cooking efficiency, whereby the high investment costs of traditional causticizing and of a soda boiler as well as the operating difficulties and risks related to the soda boiler are avoided.

As compared with known methods, the method in accordance with the invention has the difference and the advantage that formation of melt in the spent liquor gasifier is avoided. Because of the high melting point of sodium aluminate, the operation is all the time carried out in the solid phase. In addition to this, the investment costs involved in the sulphate process can be reduced significantly when using an aluminate solution by completely avoiding causticizing and by simplifying the heat recovery from the black liquor.

The invention is illustrated by the following examples.

Example 1 (comparative example)

Conventional sulphate cellulose cooking was carried out under laboratory conditions as follows:

To a 1 litre autoclave provided with a rotating mixer were added

100 g	air-dried Finnish pine chips (moisture 10 %)
12.6 g	NaOH
6.3 g	Na_2S
3.5 g	Na_2CO_3
350 g	H_2O

The autoclave was closed and cooking was carried out by raising the temperature by means of

thermostated oil firing from 20°C to 80°C during 0.5 hours and from 80°C to 170°C during 2.0 hours. The reactor was maintained at the final cooking temperature 170°C for 1.5 hours. The autoclave was cooled in one hour to 60°C.

From the autoclave, the reaction mixture was transferred to a 2 l decanter to which was added 300 g cold water, whereupon the fibres were separated from the cooking liquor by filtration. The separated cellulose fraction was washed twice with 5 litres water, whereafter the fibres were separated by filtration and dried for 12 hours at 105°C. The so washed and dried cellulose fraction was weighed, and a yield of 48.3 g cellulose was noted in the exemplary cooking. The lignin content of the obtained cellulose was determined on the basis of the so-called kappa number (TAPPI standard). Lignin content = 7.9 %.

Example 2

A test cooking was carried out under laboratory conditions where the alkali addition was dosed as sodium aluminate only. Both the sulphidity and the total alkali in the cooking liquor were the same as in the comparative cooking (Example 1).

To a heatable 1 litre autoclave provided with a rotating mixer were thus added:

100 g	air-dried Finnish pine chips (moisture 10 %)
54 g	$NaAlO_2$
12.6 g	Na_2S
3.5 g	Na_2CO_3
750 g	H_2O

The cooking was carried out by using the same temperatures as in Example 1.

Upon reaction, the reaction mixture was transferred into a 2 l decanter as in the preceding example, 300 g cold water was added and the fibres were separated from the cooking liquor by filtration. The separated black liquor was recovered for later

tests, and the cellulose fraction was washed and dried as in Example 1. The yield of washed and dried cellulose was 55.6 g, the kappa number 66.2, and the corresponding lignin content was 9.9 %.

Example 3

A test cooking according to Example 2 was carried out by using 100 g air-dried birch chips (moisture 9 %) in stead of pine chips. After washing and drying, the yield of cellulose was found to be 54.0 g, the kappa number was 36.9, and the corresponding lignin content was 5.5 %.

The black liquor separated after cooking was recovered for further tests.

Example 4

The black liquor sample separated in the two preceding examples 2 and 3 was concentrated and treated for regeneration of the cooking chemicals in the following manner.

After concentration, the composition of the black liquor was:

43.2 g	organic matter of which 9 % was sodium (3.9 g)
15 g	$Al(OH)_3$
3.2 g	Na_2SO_4
0.56 g	NaOH
0.2 g	Na_2S
80 g	H_2O

The above-mentioned black liquor sample was dried at 110°C, whereby 61.5 g dry substance was obtained. 50 g of this dry substance was crushed and heated in a gasification furnace under reducing conditions (CO gas flow 30 ml/min) by raising the temperature to 800°C in 2 hours and by keeping the product for 1/2 hour at 800°C before cooling.

The gas discharged from the gasification reactor was washed by passing it through a 2-n NaOH solution (100 ml) to collect possibly liberated H_2S gas. The residue of 29 g obtained from the heating

was dissolved in 500 ml distilled water, and the undissolved carbon-containing residue was separated by filtration, dried and weighed. This undissolved residue (20 g) was heated in a porcelain crucible at 800°C to burn the carbon; the water-insoluble residue (4.9 g) obtained from the heating was assumed to be aluminium oxide (Al_2O_3).

The water-soluble portion of the residue obtained from the heating was analysed. It was found that the aqueous solution contained no carbonates and that the Na_2SO_4 quantity dissolved therein was 0.16 g, corresponding to about 6 % of the original sulphate quantity of the sample.

The Na_2S content of the solution was determined by titration. The solution was found to contain 1.2 g Na_2S, which corresponds to 2.2 g Na_2SO_4 (of the original quantity of 2.6 g Na_2SO_4). A hydrogen sulphide quantity corresponding to 0.2 g sodium sulphate was found in the sodium hydroxide washing solution. The missing sulphur obviously had been discharged as hydrogen sulphide along with the gas flow.

The total alkali of the solution was titrated. From this was deducted the share of sodium sulphide, whereby the alkalinity was found to correspond to 0.087 mol NaOH. According to this, 7.1 g Na Al O_2 was dissolved in the solution (the excess aluminium hydroxide was present, as was already stated previously, in the insoluble residue after heating as Al_2O_3).

According to the foregoing, the composition of the part dissolved in water after gasification was:

7.1 g	$NaAlO_2$		54 g
0.16 g	Na_2SO_4	x 7.6	1.2
1.3 g	Na_2S		10.4

which almost exactly corresponds to the cooking chemical composition used in Examples 2 and 3.

Example 5

An experiment in accordance with Example 4 was carried out, in which the gas discharged from the reactor was washed for the recovery of H_2S, by first passing the gas through an aluminate solution (200 ml), whose composition was

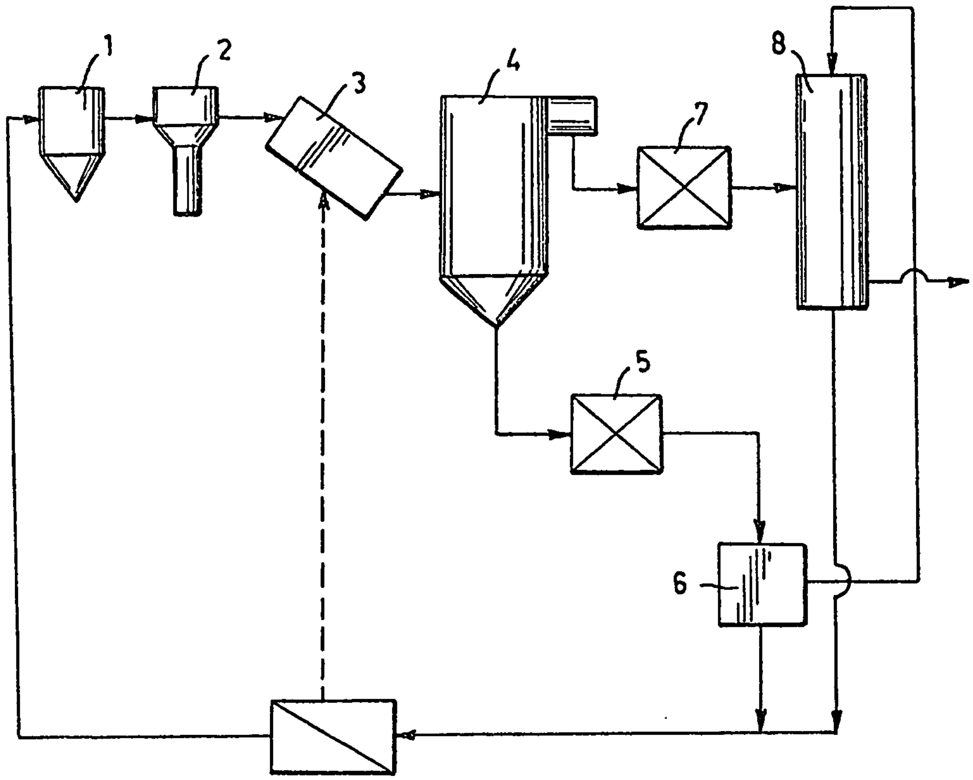
14 g Na AlO_2
0.4 g Na_2SO_4
200 g H_2O

and hereafter through a 2N NaOH solution (100 ml).

The solutions were analysed after the experiment, whereat it was noticed that the sodium aluminate solution contained a quantity of sodium sulphide (hydrogen sulphide) corresponding to 0.3 g sodium sulphate. In the other washing solution (2N NaOH), no sulphur was detected.

WHAT IS CLAIMED IS:

Method for the preparation of pulp and for the recovery of chemicals, whereby hardwood or softwood chips are cooked by means of a sodium-sulphide-containing aqueous solution of sodium aluminate in a conventional sulphate pulp cooker under standard conditions, c h a r a c t e r i z e d in that the spent liquor separated from the cooking is, after evaporation, fed into a gasifier, wherein the temperature is 700 to 1250°C, the hot inorganic matter is removed out of the gasifier, cooled by means of the air required for the gasification, crushed and dissolved in water, and the alkaline aluminate solution obtained is used as an absorption solution for the H_2S contained in the gas generated in the gasifier, whereby a solution is obtained which contains 1 to 4 per cent by weight of Na_2S and NaHS as well as 5 to 20 percent by weight of $NaAlO_2$ and which is as such, without separate causticizing, suitable for the cooking of pulp, and the obtained gas, free from hydrogen sulphide, is burned in a suitable boiler.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